Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-1138-RC2, 2020

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Chemical loss processes of isocyanic acid, HNCO, in the atmosphere" *by* Simon Rosanka et al.

Anonymous Referee #2

Received and published: 9 March 2020

General comments:

The authors describe computational chemistry calculations of HNCO with major atmospheric oxidants, including OH, NO3, Cl, and O3, using reliable methods, specifically CCSD(T)/CBS(DTQ)//M06-2X/aug-cc-pVTZ. The authors' conclusion corroborates with previously known conclusions, that the gas phase chemistry is not important for HNCO's lifetime. Then, the authors use the ECHAM/MESSy Atmospheric Chemistry (EMAC) model to evaluate global concentrations of HNCO from update biomass burning inventories. The modelling effort is particularly useful for understanding which populations may be at risk of exposure. I commend the authors on this work, and on updating the model with the latest sources of HNCO and rate constants. This modelling effort is valuble to the community and appropriate to Atmos. Chem. Phys..

The work is done with reliable methods, and the conclusions, although not novel, are robust. I appreciate the authors' systematic approach of considering all possible sites of reactions even if highly improbable (for example, page 7, lines 9-10). A criticism I have is a lack of depth in the interpretation of the results (I've highlighted some specific examples below). There is also a lack of synergy between the computational data and the model; these 2 studies seem to be separated and the authors can improve their manuscript by clarifying the importance of reporting these two methods together. Was any data used in the model coming from the computational chemistry relative energies?

My second criticism is the revisiting of the gas phase reactions of an electrophile (HNCO) with other electrophilic oxidants. The tone of the manuscript suggests that the authors were surprised by this finding (for example the text on page 7 lines 1-4), when in reality is makes sense (and was known) that these oxidants would not be important for the fate of HNCO. I'm curious to know which hypothesis the authors were testing with their gas phase mechanism computational chemistry study and why they sought to do these calculations (other than it hadn't been done before).

In general, I would recommend that the authors justify their choices of methods more clearly, to help make the methods more accessible. Although it's a strength of the work to have combined computational chemistry and atmospheric chemistry modelling, it is also not typical that one has experience with both these methods. To improve the paper, a clearer description of the methods as well as a comparison with previous works would be highly beneficial for the reader. For example, how does the authors' work compare with computational methods with other techniques (basis sets) used in atmospheric chemistry such as (Møller et al., 2016; da Silva, 2013).

Finally, I would also recommend to the authors to add quantitative data throughout discussion of the manuscript by reporting values when possible. It's always best in scientific communication to be as precise as possible (specific examples are given below).

Specific comments:

Title:

The title can be better representative of the work. First, the mention of the gas phase loss processes would be very important. It should also be highlighted that the work is theoretical and modelling. A title along the lines of, “Gas phase chemical losses processes of isocyanic acid (HNCO) investigated through computational chemistry and chemical fate transport modeling” would better represent the work. One could also consider highlighting the sources of HNCO investigated, ie. biomass burning.

Abstract:

There is a missing introduction in the abstract to the significance of HNCO. The authors should add three to five sentences stating the research problem, then the research gap and finally their methods and findings.

I would also encourage the authors to be more specific in their abstract in order to better represent the content of the article. For example, page 1, line 19 should specify which global model is being used.

I would also encourage the authors to end their abstract with a summarizing sentence and an outlook.

Introduction:

Page 1, line 28: Why is the Wentzell reference used here? There were other references prior to this work identifying HNCO in the atmosphere. See (Roberts et al., 2010; Veres et al., 2010).

Page 1, line 31: the monomer is presentative of what? A structure? A conformer? And isomer? Or did the authors mean to write “representation of the chemical structure”?

Page 1, lines 29-32: In general, these sentences are very vague. Which concentrations, which impurities? Can the authors quantify “fairly stable” with numbers and

chemical and physical properties?

Page 1, line 33: it would be important here to specify which type of modeling study (model, year, sources) was done by Young et al. The Young et al. study is an important precursor the authors’ work and more emphasis should be given to comparing this study throughout the manuscript.

Page 2, line 1: “highly toxic” is not a claim one can make based on the uncertainty between the current medical literature and a lack of exposure studies. If the authors note that 1ppbv is potentially toxic, they can explain that this number is based on thermodynamic partitioning and is not a number from empirical studies. I would revise this statement in the text.

Page 2, lines 13-15: for an additional reference for the oxidation of nicotine as a source of HNCO, see (Borduas et al., 2016a). The Hems et al. reference should be solely for cigarette smoke. The oxidation of amide references should be (Barnes et al., 2010; Borduas et al., 2015; Bunkan et al., 2015). It would be interesting for the authors to highlight the relevance of their calculations for indoor air vs outdoor air chemistry.

Page 2, line 16: The Leslie et al. review is referenced here, but best to reference the specific studies looking at these materials. See (Jankowski et al., 2014, 2016, 2017)

Page 2, line 22: these references should either be solely the review, or each study should be described. Also consider looking at (Wren et al., 2018).

Page 2, line 30: remove the word “very”. I would argue that we have a good understanding of the gas phase fate of HNCO, corroborated by this manuscript.

Page 2, line 34: I think it’s worth explaining in one or two sentences why the current data is only from elevated temperatures. Isn’t because these reactions are all negligible at room temperature?

Page 3, lines 1-3: the authors state that there currently exists no computational data on the reactivity of NO3, Cl and O3 with HNCO. Although this statement is true, why would

one expect these oxidants to react or to be important for the fate of HNCO? Based on our current knowledge of the electrophilic nature of the carbon atom in HNCO, none of these oxidants would favorably react with HNCO. Can the authors state their hypotheses (similarly to comment in the general section)?

Page 3, line 3: specify which co-reactants

Page 3, lines 4-5: the authors correctly identify the lack of knowledge and of measurements of the dry deposition of HNCO. An extended discussion on this topic is perhaps warranted. Can the authors address this important piece of missing information with their work?

Page 3, lines 7-14: the discussion on photolysis needs to be re-considered. Isn't the reason why HNCO' absorbance is only reported below 262 nm? Isn't because it doesn't absorb at higher wavelength? By this definition, one would not expect photolysis of HNCO to occur in the troposphere. The way the text is currently written suggests missing information. . .

Page 3, line 18-19: could be worth adding the values of KH here.

Page 3, lines 21-22: The most up-to-date calculations are arguably from (Borduas et al., 2016c; Roberts and Liu, 2019).

Methods:

Page 3, line 36: can the authors further justify their choice of basis set?

Page 4, lines 7-8: how was the tunneling correction of 1.5 calculated (perhaps also add a reference)?

Page 4, lines 15-16: I'm curious about the authors' reasoning for doing calculations despite all these reaction channels being negligible at room temperature. This point goes along with my point above which hypothesis were the authors starting with.

Page 4, paragraph on global modelling: a hierarchal diagram of the model would be

useful for visualization and interpretation of the components and subcomponents of the model. This figure could go either in the main text or in the supplementary information.

Page 4, lines 25-26: what is the implication of these grid sizes on the interpretation of the results?

Page 4, line 29: why were aromatics and terpenes excluded?

Page 4, lines 31-32: have the authors considered using SAR factors for amines and amides? (see (Borduas et al., 2016b))

Page 4, lines 37-38: this conclusion would certainly depend on the scale of the modelling correct? As cigarette smoke and cooking on a very local scale could also rival biomass burning, or am I wrong?

Page 4, line 38: specify the two emission factors.

Page 5, line 2: In light of (Carter et al., 2020)'s conclusions, could the authors comment on the uncertainty of their inventory.

Page 5, line 10: the chosen years are 2010-2011. Can this choice be justified? (Young et al., 2012) used 2008 fire emissions. Can these two years be compared? Why or why not?

Results

Figure 1: Overall, this figure is particularly well done and clear. I congratulate the authors here! The structures are also done well, using ChemDraw. Actually, could all the structures be drawn with bonds and bond angles similarly to the products with ozone? In addition, where are the energies of the pre-complexes?

Page 6, line 14: could the authors show graphically on Figure 2 the mentioned experimental uncertainty?

Page 6, line 15: to be more accurate, please give the range instead of an average

factor.

Page 6, line 18: specify the kinetic model.

Page 6, lines 26-27: Good conclusion, I would highlight this statement better in the abstract for example.

Page 7, line 15-16: define why an acyl chloride is less “stable” than a carboxylic acid? The current statement is rather vague.

Page 7, lines 17-18: I think this statement is wrong. Isn’t it also true for HNCO + O3 based on Figure 1? It is also inconsistent with conclusions on page 8, lines 1-3

Page 8, line 6: the Cl concentration is incorrect. See (Riedel et al., 2012) for example (concentrations of 10s to 100s ppt level). A ratio of OH/Cl of 200 appears to be typical in urban regions based on (Young et al., 2014).

Page 8, line 17: explain what is meant by “greater stability” of nitric acid.

Page 8, lines 26-27: doesn’t the sentence on lines 27-28 contradict the preceeding statement?

Page 8, line 37: specify which atoms have the reported bond energies. O-O or H-O?

Page 9, line 16: specify which mechanisms are “the described mechanisms”. There are many mechanisms reported in this work.

Page 9, line 18: be consistent with writing out the name of isocyanic acid and using the molecular formula HNCO.

Page 9, line 21-22: would be interesting to show this result/data. How was this number obtained?

Page 9, lines 33-34: it would be very important to expand this sentence into a whole paragraph for comparison. And if the argument on lines 34-35 are true, then which contribution (percentage for example) is formamide a source of HNCO? This value

could be very important for the gas phase atmospheric community.

Page 9, lines 36-37: specify which heterogeneous loss terms.

Page 10, lines 1-2: this lifetime is calculated based on which values?

Page 10, lines 5-7: interesting calculation. How do the authors interpret that number with the observed diurnal profiles in (Roberts et al., 2014)?

Page 10, line 7: did the authors consider photolysis as a sink in the stratosphere? Refer to the discussion on photolysis on page 3.

Page 10, lines 12-14: show this result graphically. It is particularly interesting.

Page 10, lines 25-27: What is the role of the model’s resolution in this analysis?

Page 11: useful graphic and table. Could the authors also add a column to their table relating to their own results? What is the implications of modelling different years of fire inventories when comparing the results in Table 1? I would also be consistent with significant figures throughout the table.

Page 11, line 8: is the wrong reference used here? Should it be Kumar et al 2018?

Page 12, starting at line 5: I would move this section before the global modelling data to help with the flow of the manuscript.

Page 12, line 11: describe RAPRNOx

Page 12, lines 21-22: unclear statement. What is being referred to as “total rate coefficients”?

Page 12, lines 28-29: why not be consistent with p6, line 5 with 298K?

Conclusions:

Page 13, lines 18-19: 5 Gg/y out of (insert number of total losses).

Page 13, line 19: first time ammonia is mentioned in the conclusion – the authors

can refer to (Leslie et al., 2019) for a back of the envelop calculation on ammonia budget from HNCO. How was ammonia implemented into the model? This discussion is rather important for the fate of HNCO and I would encourage the authors to discuss these numbers in the text as well.

Page 13, lines 28-30: this sentence appears to be out of place, and outside the scope of this work. Unless a connection with the authors' HNCO modeling can be made?

Technical comments:

Reference of SUVA should have the acronym written out.

Page 1, line 28: what is meant by "first recognized"? First studied? First synthesis? I would encourage the authors to be more precise.

Page 2, line 21: instead of "slippage" did the authors means "seepage" (especially for gas seeping out)?

Page 2, line 36: remove the word "very"

Page 3, line 5: bets to remove the word "recent".

Strangely enough, the numbers reported in the text do not match the numbers in the figure. Could the authors double check the numbers on: Page 5, line 24; page 5, line 26 (2 numbers); page 7, line 12.

Page 9, line 23: should be written HNCO (not HCNO).

Page 13, line 15: remove the word "fairly".

References: Barnes, I., Solignac, G., Mellouki, A. and Becker, K. H.: Aspects of the atmospheric chemistry of amides, ChemPhysChem, 11(18), 3844–3857, 2010. Borduas, N., da Silva, G., Murphy, J. G. and Abbatt, J. P. D.: Experimental and theoretical understanding of the gas phase oxidation of atmospheric amides with OH radicals: kinetics, products, and mechanisms, J. Phys. Chem. A, 119(19), 4298–

4308, doi:10.1021/jp503759f, 2015. Borduas, N., Murphy, J. G., Wang, C., da Silva, G. and Abbatt, J. P. D.: Gas Phase Oxidation of Nicotine by OH Radicals: Kinetics, Mechanisms, and Formation of HNCO, Environ. Sci. Technol. Lett., 3(9), 327–331, doi:10.1021/acs.estlett.6b00231, 2016a. Borduas, N., Abbatt, J. P. D., Murphy, J. G., So, S. and da Silva, G.: Gas-Phase Mechanisms of the Reactions of Reduced Organic Nitrogen Compounds with OH Radicals, Environ. Sci. Technol., 50(21), 11723–11734, doi:10.1021/acs.est.6b03797, 2016b. Borduas, N., Place, B., Wentworth, G. R., Abbatt, J. P. D. and Murphy, J. G.: Solubility and reactivity of HNCO in water: insights into HNCO's fate in the atmosphere, Atmospheric Chem. Phys., 16(2), 703–714, doi:10.5194/acp-16-703-2016, 2016c. Bunkan, A. J. C., Hetzler, J., Mikoviny, T., Wisthaler, A., Nielsen, C. J. and Olzmann, M.: The reactions of N-methylformamide and N,N-dimethylformamide with OH and their photo-oxidation under atmospheric conditions: Experimental and theoretical studies, Phys. Chem. Chem. Phys., 17(10), 7046–7059, doi:10.1039/C4CP05805D, 2015. Carter, T. S., Heald, C. L., Jimenez, J. L., Campuzano-Jost, P., Kondo, Y., Moteki, N., Schwarz, J. P., Wiedinmyer, C., Darmenov, A. S., Silva, A. M. da and Kaiser, J. W.: How emissions uncertainty influences the distribution and radiative impacts of smoke from fires in North America, Atmospheric Chem. Phys., 20(4), 2073–2097, doi:https://doi.org/10.5194/acp-20-2073-2020, 2020. Jankowski, M. J., Olsen, R., Nielsen, C. J., Thomassen, Y. and Molander, P.: The applicability of proton transfer reaction-mass spectrometry (PTR-MS) for determination of isocyanic acid (ICA) in work room atmospheres, Environ. Sci. Process. Impacts, 16(10), 2423–2431, doi:10.1039/C4EM00363B, 2014. Jankowski, M. J., Olsen, R., Thomassen, Y. and Molander, P.: The stability and generation pattern of thermally formed isocyanic acid (ICA) in air - potential and limitations of proton transfer reaction-mass spectrometry (PTR-MS) for real-time workroom atmosphere measurements, Environ. Sci. Process. Impacts, 18(7), 810–818, doi:10.1039/C6EM00312E, 2016. Jankowski, M. J., Olsen, R., Thomassen, Y. and Molander, P.: Comparison of air samplers for determination of isocyanic acid and applicability for work environment exposure assessment, Environ. Sci. Process. Impacts, 19(8), 1075–1085,

doi:10.1039/C7EM00174F, 2017. Leslie, M. D., Ridoli, M., Murphy, J. G. and Borduas-Dedekind, N.: Isocyanic acid (HNCO) and its fate in the atmosphere: a review, Environ. Sci. Process. Impacts, 21(5), 793–808, doi:10.1039/C9EM00003H, 2019. Møller, K. H., Otkjær, R. V., Hyttinen, N., Kurtén, T. and Kjaergaard, H. G.: Cost-Effective Implementation of Multiconformer Transition State Theory for Peroxy Radical Hydrogen Shift Reactions, J. Phys. Chem. A, 120(51), 10072–10087, doi:10.1021/acs.jpca.6b09370, 2016. Riedel, T. P., Bertram, T. H., Crisp, T. A., Williams, E. J., Lerner, B. M., Vlasenko, A., Li, S.-M., Gilman, J., de Gouw, J., Bon, D. M., Wagner, N. L., Brown, S. S. and Thornton, J. A.: Nitryl Chloride and Molecular Chlorine in the Coastal Marine Boundary Layer, Environ. Sci. Technol., 46(19), 10463–10470, doi:10.1021/es204632r, 2012. Roberts, J. M. and Liu, Y.: Solubility and solution-phase chemistry of isocyanic acid, methyl isocyanate, and cyanogen halides, Atmospheric Chem. Phys., 19(7), 4419–4437, doi:https://doi.org/10.5194/acp-19-4419-2019, 2019. Roberts, J. M., Veres, P., Warneke, C., Neuman, J. A., Washenfelder, R. A., Brown, S. S., Baasandorj, M., Burkholder, J. B., Burling, I. R., Johnson, T. J., Yokelson, R. J. and de Gouw, J.: Measurement of HONO, HNCO, and other inorganic acids by negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS): application to biomass burning emissions, Atmos.Meas.Tech., 3(4), 981–990, doi:10.5194/amt-3-981-2010, 2010. Roberts, J. M., Veres, P. R., VandenBoer, T. C., Warneke, C., Graus, M., Williams, E. J., Lefer, B., Brock, C. A., Bahreini, R., Öztürk, F., Middlebrook, A. M., Wagner, N. L., Dubé, W. P. and de Gouw, J. A.: New insights into atmospheric sources and sinks of isocyanic acid, HNCO, from recent urban and regional observations, J. Geophys. Res. Atmospheres, 119(Journal Article), doi:10.1002/2013JD019931, 2014. da Silva, G.: G3X-K theory: A composite theoretical method for thermochemical kinetics, Chem. Phys. Lett., 558(0), 109–113, doi:10.1016/j.cplett.2012.12.045, 2013. Veres, P., Roberts, J. M., Burling, I. R., Warneke, C., de Gouw, J. and Yokelson, R. J.: Measurements of gas-phase inorganic and organic acids from biomass fires by negative-ion proton-transfer chemical-ionization mass spectrometry, J. Geophys. Res. Atmospheres, 115(Journal Article), D23302, doi:10.1029/2010JD014033, 2010. Wren, S.

N., Liggio, J., Han, Y., Hayden, K., Lu, G., Mihele, C. M., Mittermeier, R. L., Stroud, C., Wentzell, J. J. B. and Brook, J. R.: Elucidating real-world vehicle emission factors from mobile measurements over a large metropolitan region: a focus on isocyanic acid, hydrogen cyanide, and black carbon, Atmospheric Chem. Phys., 18(23), 16979–17001, doi:https://doi.org/10.5194/acp-18-16979-2018, 2018. Young, C. J., Washenfelder, R. A., Edwards, P. M., Parrish, D. D., Gilman, J. B., Kuster, W. C., Mielke, L. H., Osthoff, H. D., Tsai, C., Pikelnaya, O., Stutz, J., Veres, P. R., Roberts, J. M., Griffith, S., Dusanter, S., Stevens, P. S., Flynn, J., Grossberg, N., Lefer, B., Holloway, J. S., Peischl, J., Ryerson, T. B., Atlas, E. L., Blake, D. R. and Brown, S. S.: Chlorine as a primary radical: evaluation of methods to understand its role in initiation of oxidative cycles, Atmospheric Chem. Phys., 14(7), 3427–3440, doi:https://doi.org/10.5194/acp-14-3427-2014, 2014. Young, P. J., Emmons, L. K., Roberts, J. M., Lamarque, J.-F., Wiedinmyer, C., Veres, P. and VandenBoer, T. C.: Isocyanic acid in a global chemistry transport model: tropospheric distribution, budget, and identification of regions with potential health impacts, J. Geophys. Res. Atmospheres, 117(Journal Article), D10308, doi:10.1029/2011JD017393, 2012.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-1138, 2020.